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Organic Amalgams: Substances with Metallic Properties Composed in Part of Non-Metallic Elements

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A. Introduction.

A great deal of evidence has been accumulated showing that complex radicals forming the positive ions of salts are metallic in nature, but hitherto the nearest approach to the actual isolation of such substances in the free state has been found in the single case of ammonium amalgam. At the suggestion of Dr. Herbert N. McCoy, to whom the author wishes to express his thanks for the many courtesies shown him during the progress of the work, an investigation having for its purpose the preparation of amalgams of positive radicals was taken up, with the hope that substances with more metallic properties than ammonium amalgam could be isolated.

The following detailed description of the experimental work is an account of the results achieved by the author, and likewise constitutes a portion of a joint paper by Dr. McCoy and himself, published in the Journal of the American Chemical Society for March, 1911.[1]

B. Preparation of Tetramethyl Ammonium Amalgam.

The first attempts at the preparation of tetramethyl ammonium amalgam were made by the action at 0° of 8 per cent. sodium amalgam on a 25 per cent. aqueous solution of tetramethyl ammonium chloride. Hydrogen was given off, but no new product resulted. The electrolysis of aqueous solutions of the chloride under various conditions of temperature and concentration gave always colloidal mercury at the mercury cathode, but no amalgam could be isolated. It was thought that an amalgam might be formed by the action of the current and be rapidly decomposed by the water. Accordingly, absolute alcohol was substituted for water as solvent and proved wholly satisfactory.

The first successful preparation of tetramethyl ammonium amalgam was accomplished by the electrolysis of a saturated solution of tetramethyl ammonium chloride in absolute alcohol, using a platinum anode and a mercury cathode. The temperature was —10°. By means of a potential-reducing device, the direct current of the lighting circuit (110 volts) was cut down to 18 volts, and the current was allowed to run at this pressure for thirty minutes. As prepared in this way, the amalgam

[1] *J. Am. Chem. Soc.*, **33**, 273 (1911).

is a stiff mixture of shining crystals of the amalgam and the excess of mercury; it is but very slightly inflated,[1] silvery white in color and decidedly metallic in appearance. In contact with alcohol it is moderately stable, but reacts violently with water.

Since this first preparation was made, the amalgam has been prepared by this method many times and many of its properties studied. However, since in using a platinum anode chlorine is evolved, the method has been improved by the substitution of an anode of silver-plated platinum gauze.

In the most convenient form of apparatus for the production of the amalgam, a small Gooch funnel is used as the electrolytic chamber. This is supported by passing the stem through a one-hole rubber stopper closing the tubulure of an inverted four-liter bell jar, which serves as an ice chamber. The whole apparatus is supported at an appropriate height, by means of a ring and a universal clamp, on an iron stand. A piece of rubber tubing fastened to the stem of the Gooch funnel, and closed by a pinchcock, affords a convenient outlet for the amalgam after it is formed. The anode consists of a piece of silver-plated platinum gauze rolled into cylindrical form. This gauze is welded to a stout platinum wire which passes between the edge of the funnel and the rubber stopper closing the funnel. The negative wire, insulated by a glass capillary tube, enters the funnel through one leg of a T tube. The upper end of this T tube, where the wire enters, is closed by means of universal wax or a glass cap and a piece of rubber tubing, while a calcium chloride tube is attached to the other leg of the T to exclude moisture. A thistle tube, reaching almost to the mercury cathode, is inserted into the second hole in the rubber stopper, and serves for the introduction of mercury or of the electrolyte.

Fitted up in this manner, the procedure for making a "run" with the apparatus is as follows: The mercury to serve as a cathode is run into the electrolysis chamber through the thistle tube; the solution of the electrolyte is then introduced, the bell jar having previously been filled nearly to the top of the Gooch funnel with crushed ice or a freezing mixture. The current is then turned on, the potential and strength being regulated so that about 0.25 ampere passes through the cell, under ordinary circumstances. After running for 10–15 minutes, the current is inter-

[1] When properly prepared, it shows at temperatures below +10° absolutely no tendency to become inflated, in which respect it differs markedly from ammonium amalgam.

rupted; the excess of mercury run off through the delivery tube at the bottom of the apparatus, into a dry dish; the amalgam is then run off into a second dry dish and used as desired, while the excess of mercury is poured, through the thistle tube, back into the electrolytic cell. In this way a number of successive runs can be made with but little interruption.

C. Properties of Tetramethyl Ammonium Amalgam.

Physical Properties.—As prepared above, at temperatures of from —10 to —5° the amalgam is a pasty, *crystallin* mass about the color of metallic zinc. While at 0° or at temperatures slightly above 0° the crystallin structure is not so pronounced, yet on several occasions almost solid lumps have been observed in the amalgam formed at 0°. It is somewhat lighter than mercury, as it always floats on the latter. There is evidence that more than one active phase exists in the amalgam. The surface tension of the amalgam is less than that of mercury. There is little tendency, from —10 to 0°, toward inflation of the amalgam, but when the temperature of a sample, washed with absolute alcohol and partially dried with filter paper, was allowed to rise slowly, the volume increased and at 25° was about twice the volume at 0°.

Stability of the Amalgam.—When the temperature of the clean amalgam is kept near 0° it is quite stable, but on allowing the temperature to rise it decomposes very rapidly. Trimethylamine is one of the products of this decomposition, as is shown by the powerful fish-like odor. The other products have not been fully investigated; it is hoped to make a further study of this point.

General Chemical Properties.—If the amalgam is run from the electrolytic cell directly into a clean, dry flask, it becomes covered with a gray-white crust, probably tetramethyl ammonium hydroxide, as it reacts with water to form an intensely alkaline solution.

The Reaction of Water on the Amalgam.—When allowed to come in contact with water a violent action takes place; hydrogen is formed and the whole of the mixture becomes ink-black, rapidly turning gray, and a gray, colloidal solution is the final result. Le Blanc[1] probably got the same substance by the electrolysis of aqueous solutions of tetramethyl ammonium chloride, using a mercury cathode—a result we have also obtained under similar conditions. We studied the phenomenon further as follows.

The amalgam was formed as usual, in the apparatus described above.

[1] Le Blanc, *loc. cit.*

After the current had been allowed to run for some time, the excess of mercury was drawn off into a clean, dry dish. The amalgam was then drawn off into a second small porcelain dish, quickly washed several times with absolute alcohol, dried with filter paper, and the dish held in the hand, against the inside edge of a 600 cc. beaker. A fine stream of water was now forcibly directed against the upper surface of the amalgam, near the lip of the dish, in such a way that the colloidal black deposit was swept into the beaker without carrying along globules of mercury. The washing with water was continued until little or no further action between the amalgam and the water was noticed. When the main portion of the "black deposit" had been swept into the beaker, in nearly every case a black, nearly solid residue, small in amount, was noticed floating on the globule of mercury left. This black substance acted less vigorously with water than the pasty amalgam, but still gave a "colloidal black deposit" with water. An explanation of this fact will be taken up later. The above outlined process was repeated a number of times, until sufficient material had been accumulated; the black residue was then filtered off through a weighed Gooch crucible, dried at 108–110° and weighed; the filtrate was reserved for further experimentation. This weighed residue was then dissolved in hot nitric acid, repeatedly evaporated with concentrated hydrochloric acid until nitric acid was practically completely eliminated, then diluted, filtered free from asbestos fibers, and the mercury precipitated by hydrogen sulfide. This precipitate was washed, dried, washed several times with carbon disulfide, dried at 108–110° and weighed. In three analyses in which from 0.4 to 0.8 g. of substance was taken the percentages of mercury found were 98.06, 97.93, 96.98.

These low but consistent values of the mercury content of the black deposit mean that the substance is in all probability the pure element, the low values being due either to (1) water absorbed to a slight degree, or (2) to a little occluded hydrogen. Less plausible would be the assumption that (1) the deposit is a mixture of mercury and mercurous oxide, or (2) that it is a compound containing the tetramethyl ammonium radical. The deposit after drying generally aggregated into actual globules, and the portion which did not do so became silvery white in color; this disposes of the first assumption, and there is no other evidence in favor of the second. The mercury itself, used in the preparation of the particular amalgams from which the black deposit was obtained for analysis, was, by analysis, 99.86 per cent. pure. The nature of the impurity was not determined.

The filtrates from each o the above experiments and a number of others were titrated with standard hydrochloric acid; the results were calculated to $N(CH_3)_4$ and the ratio, $N(CH_3)_4$ to Hg, was determined from these results, and from the weight of the colloidal mercury. In the table below, in the experiments in which the values "calculated weight, $N(CH_3)_4Cl$" and "actual weight, $N(CH_3)_4Cl$" are given, the solutions after titration were actually evaporated to dryness, and the residues weighed. These residues were then combined, purified and analyzed as shown below.

TABLE I.

Expt. No.	Cc. 0.1 *N* HCl.	98% Wt. colloidal Hg.	$N(CH_3)_4$ calc.	A.	Wt. res.	Calc. wt. $N(CH_3)_4Cl$.
270	4.00	0.1329	0.0297	1.66	...	...
271	2.50	0.0515	0.0186	1.02	...	...
272	9.50	0.2303	0.0705	1.21	...	...
273	5.82	0.4496	0.0431	3.87	...	...
274	12.72	0.2797	0.0943	1.10	...	...
277	7.12	0.3037	0.0527	2.13	...	...
279	18.18	0.3629	0.1348	0.99	0.230	0.199
282	11.11	0.7946	0.0823	3.57	...	...
283	15.43	1.3451	0.1143	4.35	0.180	86 34 10
285	26.17	0.3713	0.1938	0.71	0.294	061 68
288	12.28	0.4161	0.0910	1.69	0.126	·.o 9
291	35.50	0.4607	0.2630	0.60	0.395	09 ·022
292	23.71	0.4983	0.1757	1.05	0.252	o ε ··

In the column headed "A" is given the number of atoms of colloidal mercury formed for each tetramethyl ammonium ion set free. It is seen that this ratio is not constant. Four of the thirteen values, however, are close to *unity*, which may indicate a possible compound of the formula $HgN(CH_3)_4$. Since the colloid analyzed to 98 per cent. mercury, this per cent. of the *actual* weight of the colloid is used in the calculations.

In several of the experiments in which the colloidal mercury was not used for analysis, it was weighed on dried filter papers. In some cases the deposit was coagulated by the addition of sodium chloride and in others by the addition of concentrated hydrochloric acid. The latter, however, was abandoned as a coagulant since it dissolved some of the deposit, though not much. In experiments 270, 271, 272, 273, phenolphthalein was the indicator used, while in the rest of the experiments methyl orange was used.

The values in column "A" are to be taken as approximate only, as it was always difficult to remove every trace of the colloid from the

small dish to the beaker by means of wash water. Again, there was always a slight decomposition of the amalgam not due to the action of water.

As stated above, the residues of supposed tetramethyl ammonium chloride left on evaporating to dryness the solutions in experiments 279, 283, 285, 288, 291 and 292 were combined and analyzed. This analysis was made as follows: The combined residues were dissolved in water, the solution evaporated to dryness, the resulting mass taken up with absolute alcohol and precipitated with ether. From the mother liquor of this ethereal solution, a second crop of crystals was obtained and this was recrystallized from absolute ethyl alcohol. These samples were dried, and weighed portions dissolved in water and titrated with decinormal silver nitrate, using potassium chromate as indicator. 0.1290 g. of salt of first crystallization required 11.82 cc. of 0.1 *N* $AgNO_3$; 0.1044 g. of salt of second crystallization required 9.55 cc. 0.1 *N* $AgNO_3$. Per cent. Cl calculated for $N(CH_3)_4Cl$, 32.36. Found: I, 32.27; II, 32.47. The results of these two analyses, with the close agreement between the actual and calculated weights of $N(CH_3)_4Cl$, show conclusively that the amalgam contains the tetramethyl ammonium group.

Two analyses of the gas evolved when the amalgam reacts with water were made as follows: A quantity of the amalgam was run out into a small dish and quickly washed with absolute alcohol and dried as much as possible by means of filter paper. It was then decomposed by water and the gas evolved collected. This process was repeated until an amount of gas sufficient for analysis was obtained. The gas was then transferred to a eudiometer filled with mercury, measured, mixed with air, measured, exploded, and the contraction noted. Concentrated sodium hydroxide was now admitted to the tube, but no contraction resulted, hence no carbon dioxide was formed on explosion. In the first analysis 11.00 cc. of the unknown gas were used, and the contraction of the mixture on explosion was 15.30 cc., equivalent to 92.73 per cent. of hydrogen; while in the second case 6.50 cc. was the contraction when 4.6 cc. of the unknown gas were used, indicating 94.13 per cent. of hydrogen present.

These experiments should be regarded as qualitative only; no corrections were made for the vapor pressure of water; the experiments were made simply to demonstrate that hydrogen is the gas evolved when the amalgam is treated with water, and that no gas containing carbon was produced.

Reaction of the Amalgam with Aqueous Solutions of Various Salts.—A

cold concentrated solution of ammonium chloride was treated with tetramethyl ammonium amalgam. Ammonium amalgam, as shown by the inflation peculiar to this substance, was formed. *There were absolutely no indications of colloidal mercury.* Part of the same tetramethyl ammonium amalgam reacted in the usual way with water. A saturated solution of potassium chloride was treated with tetramethyl ammonium amalgam at room temperature. There was only a trace of colloidal mercury formed. After the mixture had stood for three minutes, the residual mercury was washed quickly six or seven times with water and then allowed to stand in contact with water. There was absolutely no indication of the presence of tetramethyl ammonium amalgam, but there was a slow reaction between the mercury and the water, gas being evolved. That potassium amalgam had been formed was proved by acidifying the aqueous solution with hydrochloric acid, adding a few drops of chloroplatinic acid and evaporating to dryness; the residue, when treated with water, remained for the most part undissolved; the yellow crystals were undoubtedly potassium chloroplatinate. A solution of sodium chloride, approximately three times normal strength, was treated with tetramethyl ammonium amalgam. No colloidal mercury was formed, but a quiet action ensued between the solution and the amalgam. This was allowed to continue for four minutes, then the mercury was quickly washed twelve times with cold water and covered with water. Gas was evolved for more than two hours. The resulting solution was alkaline to litmus—conclusive proof that sodium had replaced the tetramethyl ammonium group in the amalgam. Concentrated solutions of cesium and rubidium chlorides in water and thrice normal potassium chloride were each treated with parts of the same lot of tetramethyl ammonium amalgam. With the cesium chloride, violent action occurred with the formation of colloidal mercury, but the action was less violent than when pure water alone is used. With the rubidium chloride, only a little colloidal mercury was formed, and with the potassium chloride, none at all. When the experiment was repeated, using normal solutions of each salt in water, the results were in the same order, the only difference being that with potassium chloride a little colloidal mercury was formed, less, however, than with rubidium chloride.

An aqueous solution of copper sulfate of unknown concentration was treated with tetramethyl ammonium amalgam. The action was fairly violent; only a little colloidal mercury was formed. There was effervescence, and after standing fifteen minutes, the mercury was covered with

bubbles of gas. At this stage, very thin, copper-red crystals were noticed floating on the surface of the supernatant liquid. The mercury itself had a coppery color. It was washed seven or eight times with water, and showed every indication of the presence of copper amalgam. Part of it was dissolved in nitric acid, the resulting solution evaporated and ammonium hydroxide added to the *greenish* residue. The characteristic blue color of the cupri-ammonium ion was seen while some of the original mercury from which the amalgam had been formed gave absolutely no indications of the presence of copper on similar treatment.

Mercuric chloride in aqueous solutions was also treated with tetramethyl ammonium amalgam; the reduction to the mercurous state was more rapid than when pure mercury acts on mercuric chloride. Colloidal mercury was formed. The flocculent gray precipitate was filtered off and tested with ammonium hydroxide; the characteristic black color which this reagent affords with mercurous chloride was produced.

Normal aqueous hydrochloric acid acts vigorously on tetramethyl ammonium amalgam, only a little colloid, however, being formed. We have also shown[1] that the amalgam precipitates copper and zinc from alcoholic solutions of their nitrates. All these experiments go to show the complete analogy between the tetramethyl ammonium radical and an ordinary alkali metal, and will be referred to again after the consideration of further experimental work.

The Action of Alcohol on the Amalgam.—One of the first properties of the amalgam to be studied was the reaction with alcohol. The speed of this reaction was determined, approximately, at 0°, as follows: The amalgam was made in the usual way; it was washed four times with absolute alcohol and then immediately poured into absolute alcohol in a conductivity cell at 0°. The resistance of the solution was determined at definit intervals and from the values for this resistance at the various times the speed of the reaction was calculated, applying the formula for a unimolecular reaction, $k = 1/t \log_e a/(a - x)$. The mixture was, of course, stirred to insure uniformity of concentration as far as possible. If W is the resistance at the time t, and W_a is the final resistance, it is easy to show that $k = 1/t \log_e W(W - W_a)$, since the initial resistance, that of pure alcohol, is very high. Using this formula, k, the rate of formation of the tetramethyl ammonium ion when the amalgam is in contact with absolute ethyl alcohol is calculated from the results below:

[1] McCoy and Moore, *Science*, 30, 315 (Sept. 3, 1909).

TABLE II.

Experiment No. 33.			Experiment No. 35.		
Time, t (minutes).	Resistance (ohms) W.	k.	Time, t (minutes).	Resistance (ohms) W.	k.
0	61,600	..	0	15,400	..
11.5	840	0.0238	3	399	0.1136
21.5	308	0.0492	6	300	0.0708
31.5	264	0.0456	9	250	0.0686
41.5	234	0.0472	12	215	0.0648
51.5	205	0.0752	16	194	0.0563
61.5	201	..	19	173	0.0577
71.5	201	..	24	150	0.0609
81.5	201	..	29	139	0.0606
..	...	..	34	129	0.0646
..	...	..	40	117	0.0833
..	...	..	83	115	..
..	...	..	100	115	..

D. The Electrode Potential of the Electrode: Tetramethyl Ammonium Amalgam, Half-normal Tetramethyl Ammonium Chloride in Absolute Alcohol, and in Water.

The electromotive force of the electrode: tetramethyl ammonium amalgam, 0.5 N $N(CH_3)_4Cl$ in absolute alcohol, was measured, at 0°, against a decinormal calomel electrode. Measurements were made by a compensation method and were carried out both while the primary or polarizing current was running and after the amalgam had been formed and the polarizing current was cut off.

In order to make the measurements while the polarizing current was running, it was necessary very rapidly to shift the connections of the amalgam electrode from the polarizing circuit on the one hand to the measuring circuit on the other. Le Blanc[1] used for this purpose an electric tuning fork, but in the present work a remodeled electric bell gave better results as a vibrator. The gong and clapper were removed, and a platinum contact point passed through the clapper stem, so that when the armature of the bell was in motion it made contacts in such a way that the amalgam electrode was alternately in connection with the polarizing circuit and the measuring circuit. When the vibrator was at rest, permanent connection was made between the amalgam electrode and the measuring circuit.

Since the electrode potential of the amalgam was measured against a decinormal calomel electrode, both while the polarizing current was running and after it was cut off, provision had to be made for the anode

[1] Le Blanc, *loc. cit.*

of the polarizing circuit. This anode was made of silver wire, and was run between the stopper and the edge of the glass half-cell serving as container for the mercury forming the cathode. Connection between this mercury and the negative terminal of the polarizing circuit (through the circuit shifter) was made by means of a platinum wire sealed into a glass capillary filled with mercury. This capillary passed through a hole in the rubber stopper. The glass half-cells containing the amalgam and calomel electrodes were immersed in crushed ice, while the capillary portions of the cells extended over the edge of the ice bath into the "bridge" solution of decinormal potassium chloride. The mercury used in the preparation of the decinormal calomel electrode, and as a cathode in the amalgam cell, was recently purified by distillation in a vacuum. A D'Arsonval galvanometer was used in the measuring circuit. In all instances the "zero" method of measurement was used.

The compensating current in the measuring circuit was derived from two storage cells; the polarizing current was taken from the lighting circuit of the laboratory and by means of a variable resistance in parallel with the electrolytic apparatus the voltage was regulated without difficulty.

TABLE III.—ELECTROMOTIVE FORCE OF THE AMALGAM-CALOMEL ELECTRODE CELL, AT 0°.

A. Polarizing current *on*.				B. Polarizing current *off*.			
Expt. No.:	205.	206.	209.	Expt. No.:	205.	206.	209.
Time. Mins.	E. M. F. volts.	E. M. F. volts.	E. M. F. volts.	Time. Mins.	E. M. F. volts.	E. M. F. volts.	E. M. F. volts
0	0.229	0.240	0.247	0	2.6111	2.990	2.630
8	...	2.928	...	1.5	2.628	...	2.622
10	...	2.908	2.681	2	...	2.671	2.618
11	...	...	2.664	4	2.629	2.648	2.618
12	2.807	2.908	2.664	6	2.628	2.621	2.618
13	...	...	2.681	8	...	2.605	2.617
14	...	2.97	...	9	2.624	...	2.622
15	2.807	...	...	10	...	...	2.617
16	...	2.96	...	12	...	1.984	2.617
18	2.626	...	...	14	...	1.948	...
19	...	3.034	2.502	15	...	...	2.615
21	2.611	...	...	19	...	1.062	...
22	...	3.034	...	20	2.017	...	...
24	2.611	...	...	22	...	...	2.604
25	...	2.990	...	25	1.958	0.477	...
27	2.611	2.990	...	26	...	...	2.041
28	...	...	2.630	30	...	...	2.031
29	...	...	2.630	36	...	...	2.031
30	...	...	2.630	37	0.503	...	...
..	...	...	...	47	...	...	2.001

In making a measurement, the electromotive force of the two storage cells was first balanced against that of a cadmium cell. The polarizing current was then allowed to flow continuously through the half-cell in which the amalgam was to be formed, for several minutes. The connections having in the meanwhile been changed from the cadmium cell to the amalgam calomel electrode cell, the electric vibrator was set in motion, and the e. m. f. of the cell: Amalgam, 0.5 *N* $N(CH_3)_4Cl$ in absolute alcohol, 0.1 *N* KCl, 0.1 *N* calomel electrode, balanced against that of the two storage cells at intervals. After making measurements in this way for some minutes, the primary or polarizing circuit was broken, and the e. m. f. of the cell again measured at intervals. After completing this set of measurements, the current of the storage cells was again balanced against that of the cadmium element and the average of the two values of the electromotive force of the storage cells used in calculating the electromotive force of the amalgam calomel electrode cell. These two values of the electromotive force of the storage cell were always close together. The detailed results of these experiments are given in Table III.

In the series of values given when the polarizing current was cut off, the value for zero time is taken as the same as the final value obtained just before the polarizing current was cut off.

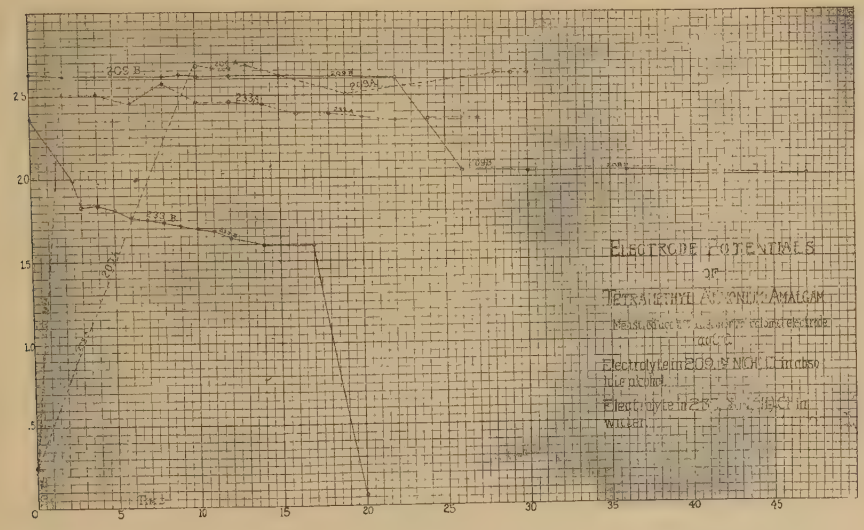

Fig. 1.

In addition to the potential measurements above, the potential of an amalgam cell using water as the solvent for tetramethyl ammonium chloride, of half-normal concentration, was determined. This set of measurements was likewise made against a decinormal calomel electrode, at zero, in a manner exactly similar to that above. The results of this experiment, with the polarizing current on (Series A) and off (Series B) are given below:

TABLE IV.

Time, min.....	0	2	2.5	4	6	8	10	12	14
Series A.....	0.219	2.507	...	2.507	2.452	2.571	2.46	2.46	2.448
Time, min.....	0	2.5	3	4	5	6	7	8	9
Series B.....	2.359	1.99	1.831	1.844	1.811	1.763	1.752	1.736	1.714
Time, min.....	16	18	20	22	24–27	...	...	...	...
Series A.....	2.387	2.387	2.373	2.352	2.359	...	...	...	...
Time, min.....	10	11	12	14	17	19	...	...	...
Series B.....	1.699	1.678	1.637	1.596	1.591	0.063	...	...	...

The curves for two experiments, Nos. 209 and 233, the one in which alcohol was the solvent, and the other, in which water was the solvent, are shown in Fig. 1.

E. Discussion of the Potential Measurements.

On examining the two curves, it is seen that their forms are very interesting. In 209 B, where the electrolyte was half-normal tetramethyl ammonium chloride, in absolute alcohol, the potential remained constant for some time after the polarizing current was interrupted. This constant value was about 2.62 volts; after awhile, however, the potential dropped rapidly to a new value near 2.00 volts.

In 233 B, with water as the solvent for the half-normal tetramethyl ammonium chloride, the average value of the potential, while the current was on, was about 2.4 volts, but on cutting off the polarizing current the potential dropped to about 2.0 volts immediately, then gradually fell to 1.6 volts, and in the end quickly dropped to almost zero.

The horizontal or nearly horizontal portions of these curves can have but one interpretation; a definit phase of the amalgam gives rise to a definit potential; and when this particular phase is exhausted, if there is a different phase possible, the potential drops to that of the new phase. Hence, in 209 (as in 205 and 206, as will be seen by plotting curves for these experiments) there were formed at least two phases: one may be the decomposition product of the other, or they may be coincident in the amalgam, the more active disappearing first.

Now, Wilsmore and Johnson[1] have recently shown that for the electrode potential of metal, using as a solvent, for the salt of the metal, liquid ammonia at —35.5°, a higher value is obtained than when water is the solvent. They account for this fact on the assumption that the degree of ionization is less in liquid ammonia than in water solutions of equivalent concentrations. This explains why, in the present instance, the electrode potential of one of the phases stable in contact with absolute alcohol solutions of tetramethyl ammonium chloride is 2.6 volts, while in contact with an aqueous solution of the same salt in equivalent concentration the potential averaged about 2.40 volts. The two values, 2.6 volts in alcoholic solution and 2.4 volts in aqueous solutions of tetramethyl ammonium chloride, are obviously due then to the same phase, but when the polarizing current is cut off where water is the solvent the potential immediately falls because this phase is very reactive towards water. Likewise, the phase showing a potential of 2.0 volts in experiment 209 must be the same which shows a potential of 1.74 volts (average) in experiment 233, but this phase is likewise less stable in contact with water than alcohol as is shown by the slowly but constantly changing values in 233 B.

The high polarization values in experiments 205 and 206 are probably due to a still more active phase which did not appear in experiment 209.

These experiments do not afford the only proof at hand that more than one phase of the amalgam is formed. Throughout this work it has been noticed that immediately under the anode the amalgam formed has a more solid, more crystallin appearance and a darker color than the rest of the amalgam; in experiment 300, a portion of amalgam practically solid was formed. Again, when the amalgam is treated with water the first action is violent and the whole of the reaction mixture becomes inky-black, quickly turning to the gray color of ordinary colloidal mercury. On treating the amalgam with water in a flat dish and washing away the colloid by means of a stream of water as fast as it is formed a darker, more solid phase, floating on the mercury, has been noticed. While this phase still reacts with water to form the colloidal mercury, it is less active than the main portion of the amalgam.

The existence of these various phases may explain why no constant values for the ratio of the colloidal mercury to the tetramethyl ammonium group have been found, as each run has obviously been a mixture of a number of phases in varying proportions.

[1] Wilsmore and Johnson, *Elektrochem. Z.*, 14, 203.

It will now be of interest to compare our results with those of Lewis and Kraus,[1] just published, on the potentials of sodium and sodium amalgam, although we made no serious attempt at accurate definition of the potentials measured, while they attained a remarkably high degree of accuracy. For the cell: Sodium amalgam (0.206 per cent.), normal Na ion, normal calomel electrode, Lewis and Kraus found an electromotive force of 2.1525 volts at 25° and for metallic sodium, normal Na ion, normal electrode, 2.9981 volts. In experiment 233, Table IV, we found for the cell: tetramethyl ammonium amalgam, 0.5 normal ion, 0.1 normal KCl, decinormal electrode, a maximum electromotive force of 2.57 volts at 0°. This would be equivalent to about 2.73 volts for conditions as in the experiments of Lewis and Kraus, excepting the concentration of the amalgam. The latter was not known in our experiment, but was probably in the neighborhood of 1 per cent. It is, therefore, clear that the potential of our amalgam is decidedly greater than that of sodium amalgam of the same concentration, which conclusion is in harmony with the very much greater activity of our amalgam toward water and alcohol.

Reuter[2] found that the potential of potassium is 0.4 volt higher than that of sodium at —80°, which would indicate a difference of 0.6 volt at 25°. As a rough estimate, then, the potential of our amalgam should be about the same as that of potassium. From the observed behavior toward water, however, we should expect the potential to exceed that of potassium, but to fall somewhat short of that of rubidium. It is of passing interest, though of doubtful significance, that the molecular weight of tetramethyl ammonium, 74.1, falls between the atomic weight of potassium, 39.1, and rubidium, 85.45.

F. Monomethyl Ammonium Amalgam.

The polarization measurements of Le Blanc[3] indicated that an amalgam was formed by the electrolysis of an aqueous solution of monomethyl ammonium chloride. We had no difficulty in obtaining the amalgam. The electrolysis took place at ordinary temperature, with 0.25 ampere. The readily formed amalgam resembled ammonium amalgam in its properties. When a solution of *dry* monomethyl ammonium chloride in absolute alcohol was electrolyzed (experiment 55) at ordinary temperature, at 0° and at —9° amalgamation again occurred. At —9° the

[1] This Journal, 32, 1459 (1910).
[2] *Z. Elektrochem.*, 8, 801 (1902).
[3] *Loc. cit.*

amalgam formed was pasty. The potential of the cell: *monomethyl ammonium* amalgam, 0.5 *N* monomethyl ammonium chloride, 0.1 *N* KCl, 0.1 *N* calomel electrode was measured, exactly as in the method above for the tetramethyl ammonium amalgam. The solvent in 229 was water and in 231 was absolute alcohol. "Series A" in each case contains measurements made while the polarizing current was on; "Series B" after the polarizing current had been cut off.

TABLE V.—ELECTROMOTIVE FORCES IN VOLTS.

Time, min.	229A.	229B.	Time, min.	231A.	231B.
0	0.023	2.369	0	0.161	1.952
1	...	1.646	..	...	...
2	...	1.655	2	...	1.372
4	...	1.666	4	...	1.314
6	...	1.666	6	...	1.340
7	...	1.670	..	...	...
..	...	...	8	...	1.318
9	...	1.623	..	...	...
..	...	...	10	...	1.323
11	...	1.569	12	2.126	1.311
13	2.099	1.556	..	...	...
15	2.099	1.504	14	2.082	1.260
17	2.153	1.512	16	1.889	0.387
19	2.153	1.481	18	1.915	0.300
21	2.335	1.481	20	1.915	0.269
23	2.282	1.471	22	1.933	...
25	...	1.471	24	1.924	...
27	2.479	1.460	27	1.952	...
28	2.369	...	..	...	...
30	...	1.455	..	...	...
33	...	1.085	..	...	...
34	...	0.842	..	...	...

On examining these results, it is seen that here the potentials in contact with alcohol are less than those where water is the solvent; it was found that a similar result was obtained with ammonium amalgam; indeed the remarkable fact was discovered that ammonium amalgam is much more reactive toward absolute alcohol than toward water.

As tetramethyl ammonium amalgam was obtained very soon after this work was undertaken, almost immediately an extensive search for amalgams of other radicals was begun, with the hope that some might be found which would be more stable. Of eighteen additional radicals studied, only one, monomethyl ammonium, gave an amalgam which could be isolated. The others gave, in general, negative results. The salts so studied were:

dimethyl ammonium chloride, trimethyl ammonium chloride, monoethyl ammonium chloride, tetraethyl ammonium chloride, propyl ammonium chloride, butyl ammonium chloride, iodomethyltrimethyl ammonium iodide, aniline hydrochloride, dimethylaniline hydrochloride, phenylenediamine hydrochloride, phenyldiazonium chloride, pyridine hydrochloride, tetraethylphosphonium iodide, tetramethylstibonium iodide, trimethylsulfinium iodide, hydroxylamine hydrochloride and hydrazine hydrochloride.

G. Summary of Results.

1. Tetramethyl ammonium amalgam has been prepared by the electrolysis in the cold of solutions of tetramethyl ammonium chloride in absolute alcohol, using a mercury cathode.

2. The amalgam exhibits certain physical properties of metals to a high degree. It has a crystallin structure more or less pronounced under certain conditions. It is lighter than mercury, but does not expand or become inflated at or below 10°, as does ammonium amalgam.

3. While fairly stable at low temperatures, near 20° it decomposes rapidly, yielding trimethylamine as one of the decomposition products.

4. In contact with cold air, it becomes coated over with a white alkaline crust, due to oxidation.

5. Water reacts violently on the amalgam, producing hydrogen, colloidal mercury, and tetramethyl ammonium hydroxide.

A study of this reaction affords evidence that more than one active phase exists in the amalgam.

6. The amalgam acts on aqueous solutions of ammonium, sodium, potassium and copper salts, and alcoholic solutions of copper and zinc salts, the tetramethyl ammonium group replacing these metals in the salts and setting free the metals themselves or forming the amalgams of these metals. With rubidium and cesium salts the action is more violent than with potassium salts of equivalent concentration, but there is replacement even in the case of the cesium salts. The tetramethyl ammonium radical possesses a solution tension comparable with that of potassium, but probably less than that of rubidium, and considerably less than that of cesium.

7. The rate of formation of the tetramethyl ammonium ion from the amalgam, in contact with absolute alcohol, is about 5 per cent. per minute at 0°.

8. The electrode potentials of the amalgam in contact with water solutions and in contact with alcoholic solutions of tetramethyl ammo-

nium salts have been measured against a decinormal calomel electrode at 0°.

2.6 volts and 2.0 volts were the values of the electromotive force of the amalgam calomel electrode cell found in contact with alcoholic solutions; 2.4 and 1.7 volts were found in contact with aqueous solutions of tetramethyl ammonium salts as the values of these potentials. The two values in each case probably correspond to two phases, thus substantiating other evidence that more than one phase of the amalgam is present in the amalgam. The curves for these potentials have been plotted.

9. Besides the extensive work upon tetramethyl ammonium amalgam, search has been made for other possible amalgams. Of the substances investigated, the monomethyl radical yields an amalgam, and the potential of this amalgam against a decinormal calomel electrode has been measured. This amalgam, like ammonium amalgam, is less stable in contact with alcohol than with water. The dimethyl ammonium radical, according to potential measurements, may possibly form an amalgam under certain conditions. Tetraethyl ammonium probably forms a very unstable amalgam. Of all the other substances investigated, a number gave faint indications of amalgam formation, but none gave as positive results as the three substances mentioned above.

10. As set forth in the introduction, we have proposed the hypothesis that complex radicals, constituting the positive ions of salts, if electrically neutralized by the introduction of electrons, equal in number to the valence of the ion, will be substances having metallic properties. We have, however, given some reasons why it may be impossible to isolate such radicals. While our experiments have not yet led to the complete isolation of complex radicals, we have gotten a new amalgam of one such radical which is far more stable than either ammonium amalgam or monomethyl ammonium amalgam. Though this substance is a compound of carbon, hydrogen and nitrogen on the one hand and mercury on the other, it has true metallic properties. Inasmuch as ordinary binary alloys with true metallic properties are formed only from components which are *both* true metals we are warranted, we think, in concluding that the organic radicals in our amalgams are in the metallic state and, therefore, that *it is possible to prepare composit metallic substances from non-metallic constituent elements*.